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硕 士 学 位 论 文

九龙江河口沉积物中汞的时空变化研究

Study on temporal and spatial variation of mercury in sediments of Jiulongjiang Estuary

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摘　要

汞是一种可全球循环的持久性有毒污染物。在全球对汞污染状况越来越重视的大背景下，作为福建省第二大河流以及厦漳地区主要水源地的九龙江的汞污染理应受到更多关注。厦门 SY 电厂是九龙江河口区域内汞污染的重要点源，对其周边海域沉积环境进行长期监测并作综合评价，是十分必要的。常规的汞浓度及形态分析法在汞污染的溯源及追踪方面显得无能为力，而近年来兴起的稳定同位素分析技术，为深入研究汞污染源及迁移转化提供了新方法。

本文以九龙江河口为研究区域，探讨沉积物中汞的污染特征，解析汞的来源，主要内容和结果如下：

（1）在福建龙海九龙江口红树林省级自然保护区的林内和林外光滩，各采集一根柱状沉积物样；对其中的总汞、甲基汞、汞同位素、总有机碳以及铅定年等参数进行测定，分析污染累积特征。结果显示：光滩柱状样总沉积时间为 32 年，沉积速率转折点发生在 1992 年左右，即该地自 1992 年起水文特征发生较大变化。林内柱状样的沉积受到较大干扰，无法得到准确的定年信息。光滩柱状样的总汞浓度范围为 116.0~435.3 ng/g，均值 190.8 ng/g；甲基汞浓度范围为 0.18~0.52 ng/g，均值 0.26 ng/g；甲基汞占总汞比值的范围为 0.11%~0.20%，均值 0.14%。林内柱状样的总汞浓度范围 71.75~145.5 ng/g，均值 121.3 ng/g；甲基汞浓度范围 0.39~1.03 ng/g，均值 0.58 ng/g；甲基汞占总汞比值的范围为 0.36%~0.71 %，均值 0.47 %。总体上，林内柱状样的总汞浓度比光滩的低，甲基汞浓度比光滩的高。林内柱状样中甲基汞浓度和甲基汞占总汞比值随采样深度的增加呈现先增后降的趋势。两根柱状样中的汞同位素均发生了明显的负的质量分馏（Mass dependent fractionation, MDF），光滩所受的人为源的影响更大。据分析，光致还原反应是光滩柱状样中汞同位素非质量分馏（Mass independent fractionation, MIF）的主要因素。总汞含量与有机碳含量并无显著相关性，说明总有机碳可能不是研究区域内影响汞甲基化的主要因子。

（2）在九龙江河口区沿河端向海端采集 10 个站位的表层沉积物样；对其中的总汞、汞同位素、总有机碳以及硫化物进行测定，解析汞的来源。结果显示：

河口区表层沉积物中总汞浓度位于 24.8~140.4 ng/g 范围内，均值为 100.9 ng/g，汞污染水平较低。总汞与总有机碳成显著正相关关系，与硫化物无相关性，说明总有机碳是研究区域内影响总汞含量的主要因子，硫化物的影响弱于总有机碳。δ^{202}Hg 介于-1.86‰~0.11‰之间，均值-0.74‰；Δ^{199}Hg 介于-0.10‰~0.11‰之间，均值 0.03‰；Δ^{201}Hg 介于-0.01‰~0.54‰之间，均值 0.34‰。沉积物中存在负的汞同位素 MDF 和正的奇数汞同位素 MIF，光致还原反应对表层沉积物中汞同位素 MIF 的贡献率较大。表层沉积物及悬浮颗粒物的汞同位素组成特征不尽相同，说明沉积物中汞 MDF 特征并不能完全反映其同站位颗粒物的汞 MDF。汞的二元混合模型的应用结果说明 SY 电厂并非本研究区域唯一的汞污染人为源。九龙江河口区的汞污染很可能来自多个点源甚至是面源。

（3）根据本课题组自2008年冬季至今对厦门SY电厂脱硫海水排放海域的长期监测数据，综合分析该海域表层沉积物中汞污染，评价SY电厂脱硫海水对海域沉积物中汞含量的影响。结果显示：SY电厂脱硫海水排放海域各长期监测站位的总汞浓度无明显的季节变化，排水口的总汞浓度略高于参考点。监测站位汞的生态危害系数很高，大部分具有很强的生态危害，该海域环境的潜在生态危害不容小觑。

关键词：各形态汞；汞同位素；九龙江河口；柱状沉积物；表层沉积物

ABSTRACT

Mercury (Hg) is a persistent global cycle toxic pollutant. More and more attention has being paid to the global Hg pollution. Jiulongjiang River is the second largest river in Fujian Province, as well as the major drinking water source of Xiamen and Zhangzhou. Hg pollution in Jiulongjiang River deserves more concerns. Xiamen SY power plant is an important point source of Hg pollution at Jiulongjiang Estuary, thus long term monitoring and comprehensive evaluation of the sedimentary environment in its adjacent sea area is necessary. The traditional methods of concentration and speciation of Hg cannot meet the requirement of Hg sources tracking. However, technique of stable isotope analysis opens a way out. It provides a new method for further study of source, migration and transformation of Hg.

In this study, the Jiulongjiang Estuary was chosen as the study area to explore the pollution characteristics and analyze the sources of Hg in sediments. The main contents and results are as follows:

(1) A study was carried out to investigate the characteristics of cumulative pollution in core sediments collected from inside and outside of a mangrove forest located in Longhai, Jiulongjiang Estuary. Total mercury (THg), methyl mercury (MeHg), Hg isotopes, total organic carbon (TOC) and $^{210}Pb_{ex}$ were determined. Total deposition time of bare flat (G) core was 32 years. The turning point of deposition rate occurred at about 1992, suggesting that the hydrological characteristics of the site had a change at 1992. Mangrove (H) core suffered obvious interference during the deposition process, showing no accurate dating information. In core G, concentrations of THg were in a range of 116.0~435.3 ng/g, with an average of 190.8 ng/g; MeHg ranged in 0.18~0.52 ng/g, with an average of 0.26 ng/g; the ratio of MeHg/THg was between 0.11%~0.20%, and average was 0.14%. In core H, concentrations of THg were between 71.75~145.5 ng/g, with an average of 121.3 ng/g; MeHg 0.36~1.03 ng/g, average 0.58 ng/g; the ratio of MeHg/THg 0.36%~0.71%, average 0.47%. Overall, THg concentration of core H was lower than that of G, while MeHg concentration of core H was higher than that of G. The concentrations of THg and the

ratio of MeHg/THg in core H firstly increased and then decreased as the sampling depth increased. Obviously negative mass dependent fractionation (MDF) and significant mass independent fractionation (MIF) of odd Hg isotope were observed in both cores. Core G suffered a greater impact of anthropogenic sources. The Hg MIF of G was mainly due to photoreduction reaction. Correlation analysis found that in the cores the THg and MeHg concentration had no signification correlation with TOC, indicating that TOC might not be the main factor impacting Hg methylation in the study region.

(2) THg, Hg isotopes, TOC and sulfide had been determined in surface sediments collected from 10 stations at Jiulongjiang Estuary for analyses of sources of Hg. The concentrations of THg were in a range of 24.8~140.4 ng/g, with an average of 100.9 ng/g, showing low level of Hg contamination. Correlation analysis found that the THg concentration had signification positive correlation with TOC but no correlation with sulfide. The data meant that TOC could be the main factor impacting THg concentration in the study region, and the impact of sulfide was weaker than TOC. The value of δ^{202}Hg ranged in -1.86‰~0.11‰, with an average of -0.74‰; and Δ^{199}Hg was in -0.10‰~0.11‰, average 0.03‰; and Δ^{201}Hg in -0.01‰~0.54‰, average 0.34‰. The isotope analysis results showed that negative MDF and positive MIF of odd Hg isotope existed in the sediments. Photoreduction reaction was the main reason of the Hg MIF. The difference of Hg isotope compositions between surface sediments and suspended particles indicated that the MDF of Hg in sediment was not equal to that in the suspended particles collected from the same station. The application of Hg binary mixture model presented a result that SY power plant was not the only anthropogenic source of Hg pollution in the study area. Hg pollution in Jiulongjing Estuary is likely to derive from multiple point sources and even surface sources.

(3) Based on the long term monitoring data of the sea area near the discharging outlet of the desulfurized seawater from SY power plant since winter 2008, a comprehensive analysis of Hg pollution in surface sediments was carried out to assess the impact of Hg concentration in desulfurization seawater on the nearby sea

sediments. The THg concentration of both two monitoring stations had no significant seasonal variation. THg concentration at the discharging outlet was slightly higher than that at a reference point. High ecological risk index were ranked for the long term monitoring stations, and most of them showed a strong ecological hazard. Potential ecological harm to the marine environment should not be underestimated.

Keywords: Various forms of mercury; Mercury isotopes; Jiulongjing Estuary; Core sediment; Surface sediment

缩略语表

CFCVG	Continuous flow cold vapor generation	连续流冷蒸气发生
EPA	Environmental Protection Agency	环境保护署
MC-ICP-MS	Multi-collector inductively coupled plasma mass spectrometer	多接收器电感耦合等离子体质谱仪
MDF	Mass dependent fractionation	质量分馏
MeHg	Methyl mercury	甲基汞
MIE	Magnetic isotope effect	磁同位素效应
MIF	Mass independent fractionation	非质量分馏
NVE	Nuclear volume effect	核体积效应
PFA	Polyfluoroalkoxy	可溶性聚四氟乙烯
THg	Total mercury	总汞
TOC	Total organic carbon	总有机碳
UNEP	United Nations Environment Programme	联合国环境规划署
WHO	World Health Organization	世界卫生组织

第 1 章 绪 论

1.1 汞的性质及危害

汞，相对原子量 200.59，位于元素周期表第六周期、第ⅡB 族。汞是地壳中相当稀少的一种元素，丰度约为 7 ng/g[1]，自然界中罕见于金属单质，常见于朱砂、氯硫汞矿、硫汞锑矿和其他矿物，其中以朱砂最为常见。汞是在常温、常压下呈液态的唯一重金属，易流动，易挥发，且温度越高挥发量越大。汞的化学性质较稳定，不能从酸溶液中置换出氢，但容易与除铁以外的大部分普通金属形成合金，这些汞合金统称汞齐[2]。其中金汞齐常用于炼金，钠汞齐常用作有机合成中的还原剂，也被用于高压钠灯中。汞在自然界中的主要存在形式包括元素态汞、二价态汞和有机汞。

汞是高毒性物质，已被世界卫生组织（World Health Organization, WHO）、联合国环境规划署（United Nations Environment Programme, UNEP）和美国环境保护署（Environmental Protection Agency, EPA）等机构列为优先控制污染物。多种汞化合物被列入我国《剧毒物品品名表》，如氯化汞、砷化汞、氧化汞等[3]。汞可在各种生态系统中进行生物累积和生物放大，通过皮肤、呼吸道、消化道进入人体，对人体健康和环境生态安全产生重大威胁。除职业接触外，被汞污染的食物、空气、护肤品以及牙科汞合金是人体暴露于汞的主要途径。

不同形态汞的毒性差异较大。无机汞不具有脂溶性，容易排出体外，毒性相对较小。微量的氯化亚汞还可用作口服泻剂。有机汞的毒性较大，其中又以甲基汞（Methyl mercury, MeHg）的毒性最大。MeHg 易被生物吸收蓄积，富集倍数高达 10^6~10^7，对人体主要表现为神经毒性和致畸作用[4]。汞中毒以慢性毒性为主，症状表现为神经衰弱综合征、汞毒性震颤、口腔炎和肝肾损伤等。低剂量长时间的 MeHg 暴露会损害神经系统。急性毒性通常表现为呕吐、气喘、心脏衰弱等症状，严重时会导致昏厥甚至死亡[5]。MeHg 易与生物大分子中的巯基结合，随血液循环系统扩散至全身，并能轻易透过血-脑屏障在脑组织中蓄积，干扰氨基酸的生化功能，造成脑部神经系统的直接损害，对孕妇、婴幼儿等脆弱群体的